ELECTRONIC STRUCTURE AND STABILITY OF HIGHER FULLERENES

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Introduction

Stability of fullerenes is one of most important questions of their research keeping in mind prospects of practical application of these new substances and materials on their basis. Therefore, a search of the laws shown in structure of stable (produced, allocated and characterized) fullerenes becomes an actual problem that will allow reaching the successes in widening of its production.

There are two principal reasons of instability of fullerenes that obeying an isolated pentagon rule (IPR) – first one is connected with open-shell fullerene molecule i.e. its radical nature, and second one is due to molecular strain, caused by its topology when molecule has a closed electronic shell. In the first case, the radical-containing fullerene structure becomes stable as endohedral metallofullerenes [1].

Here we shall consider stability of proper (or in other word "empty") higher fullerenes. The whole number of fullerenes, which obey IPR, to begin with C_{60} up to C_{84} is equal to 51, but only 17 of "empty" fullerenes are extracted and identified now, in spite of there are much more fullerenes in this row that have the closed electronic shell.

The quantum-chemical calculations play important role: the analysis has shown that all most stable fullerenes have minimal energy among their isomers. Nevertheless, the reason why one fullerene may be obtained and other one may be not, moreover is it possible to obtain it in principle - is not clear yet. To answer these questions we have carried out the analysis of total energies and standard enthalpies of formation of fullerenes that referenced to one carbon atom, based on published and our own data [2-4]. Any point of plot (fig.1) for all stable fullerenes has been bound to the point of the C_{60} fullerene. As a result the allocated sector or "beam of stability" was formed. Its top border line is defined by lowest energies and standard enthalpies of formation of fullerenes, whereas the bottom curve defines border of the highest values of energy and standard enthalpy of formation for all known stable isomers of fullerenes C_N.

Results and discussion

First of all that attracts attention is increasing of fullerene cage size or of its number of carbon atoms accompanies by steady tendency of total energy reduction (fig.1) It is obvious that it reflects the general reduction of a molecular strain of spheroid molecules passing from C_{60} to higher fullerenes.

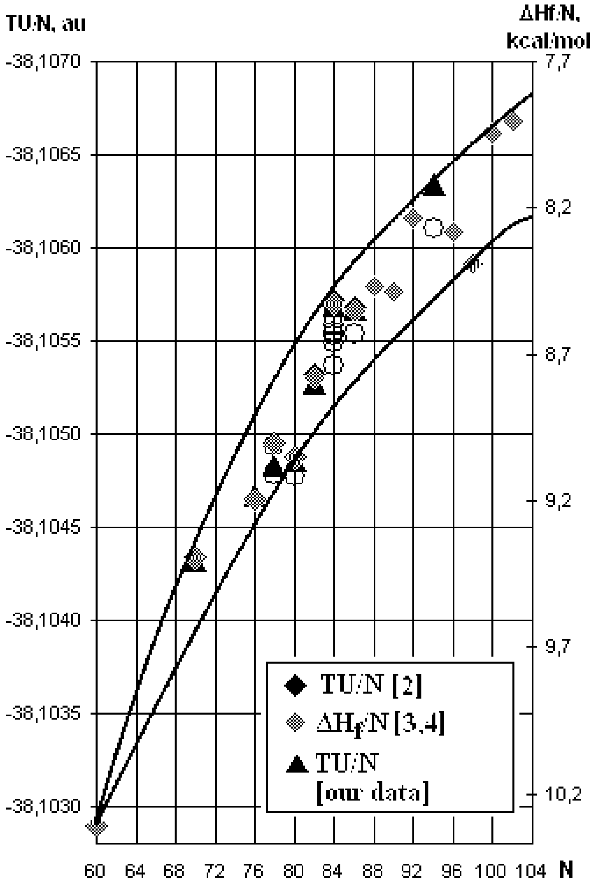

Fig.1. *Reduced total of energy (TU/N) and standard enthalpies of formation ($\Delta H_f/N$) of stable, i.e. obtained, extracted and characterized, fullerenes C_N ([2-4] and our results).*

If the most energetically favorable isomer of the fullerene is located near a top curve of a beam, it means that there is possibility to obtain other isomers which total energy (or enthalpy of formation) lay in the gap defined by distance from top up to bottom points of a beam for this fullerene. This gap reaches ~ 25 kcal/mol for fullerene C_{84}. As a matter of fact, there are ten isomers of C_{84} that extracted and characterized a difference in energy reaches up to 20 kcal/mol. We may predict, that in principle it is possible to obtain extra 5-8 isomer of this fullerene. In contrast, only two isomers of fullerene C_{80} have been extracted. Their energy difference is equal only to 5 kcal/mol, but their calculated energies lay near a bottom border of a beam, that seems make it impossible to extract other closed-shell isomers of C_{80}.

It is obvious, that in spite of some its prognostic value the discussed procedure based on integrated parameters of molecular structure does not allow judging the reason of stability of one isomer, or instability of other. The attempts to work out some criteria of stability (J. Aihara et al.) have failed, because of absence of the analysis of local stability, i.e. stability of substructures which combination makes a fullerene molecule. Synthesis of fullerenes, in our opinion, goes by a way of selection of stable substructures. However, as a rule theoretical calculations consider the molecule as a whole that seems to be a lack of the existing approach of studying of stability fullerenes.

To overcome this problem we fulfil an analysis of π-bonds distribution for all number of fullerenes from C_{60} up to C_{84}. It allowed us to identify a number of fullerene substructures that have electronic features similar to their well known aromatic analogues, such as naphthalene, indacene, pyrene, perylene, corannulene, coronene, etc. (fig.2).

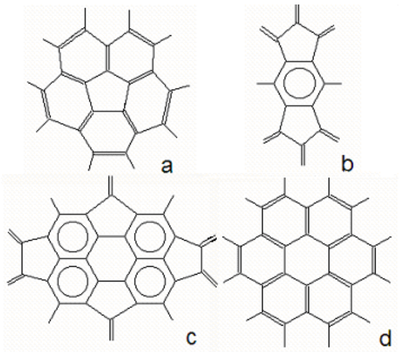

Fig.2. *Substructures, that mainly characteristic for stable higher fullerenes: corannulene (a), indacene (b), perylene (c), and coronene (d).*

These substructures keep in general their electronic state irrespective of the fact which fullerene they belong. All stable fullerenes considered include corannulene and indacene substructures that most stable fullerene C_{60} and C_{70} consist of. There are perylene and coronene substructures that present in structure of some higher fullerenes. The presence of three or more of coronene substructures is essentially destabilizing higher fullerene molecules. Anyway, the more size of fullerene cage the weaker this effect that compensates by increasing of fullerene sphere dimension.

Conclusions

The analysis of electronic structure of stable (extracted) higher fullerenes has allowed us to reveal the general rules governed their molecular structure. All stable fullerenes have the closed shell and their molecules are characterized by rather uniform pentagons distribution on a fullerene sphere. It is shown, that the opportunity of production of isomers of the higher fullerenes is defined by position of the most energetically favorable isomer on an offered "beam of stability", that have been constructed according calculated and experimental data for stable fullerenes, having the closed electronic shell.

References

1. Khamatgalimov A.R., Kovalenko V.I. Endohedral higher metallofullerenes: structure and properties. Russ. Chem. Journ. 2004, 48, № 5 : 28-36. (russian).
2. Chen Z., Cioslowski J., Rao N., Moncrieff D., Bühl M., Hirsch A., Thiel W. Endohedral chemical shifts in higher fullerenes with 72-86 carbon atoms. Theor. Chem. Acc. 2001, 106 : 364-368.
3. Cioslowski J., Rao N., Moncrieff D. Standard Enthalpies of Formation of Fullerenes and Their Dependence on Structural Motifs. J. Am. Chem. Soc. 2000, 122 : 8265-8270.
4. Chen Z., Thiel W. Performance of semiempirical methods in fullerene chemistry: relative energies and nucleus-independent chemical shifts. Chem.Phys.Lett. 2003, 367 : 15-25.